

## Method for adjusting the amount of zinc powder when removing impurities from zinc sulphate solutions

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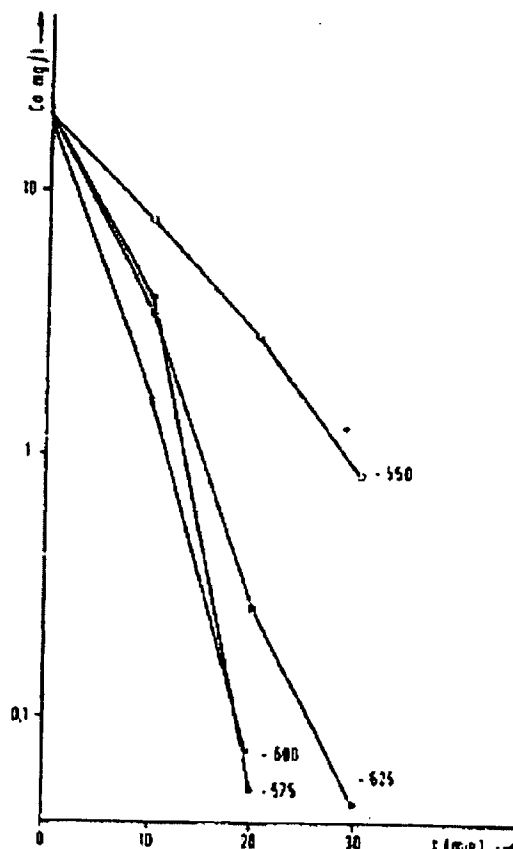
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### Abstract of DE3819020

The invention relates to the removal of impurities from zinc sulphate solution en route to electrolytic refinement of zinc, and in particular to adjusting the amount of zinc powder which is used in removing impurities. The removal of impurities such as, e.g., copper, cobalt, nickel and germanium, as well as cadmium, is carried out in such a way that they are cemented with zinc powder, a measurement of the redox potential being carried out to optimise the amount of zinc powder employed.



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The invention relates to a method to the removing impurity from zinc sulfate solutions on the path for electrolytic refining of zinc and in particular to adjusting the amount at zinc powder, which becomes used with the removing impurity. The removing impurity, like z. B. Copper, cobalt, nickel and germanium as well as cadmium become conducted, by cementing it by zinc powder, whereby the amount of the used zinc powder becomes optimized by the application of redox potential measurements.

The major raw materials used in electrolytic zinc procedures are zinc concentrates, which become first on oxidative manner calcined. The calcined product becomes in a recycled acidic, sulphuric acid contained solution dissolved, which is recovered by the electrodeposition. The insoluble components become from the zinc sulfate solution resultant with the solution process separated. The solution becomes the other solution cleaning supplied, whereby all nobler elements than zinc become remote. After the solution cleaning the solution of the electrolysis becomes supplied.

The raw solution of a zinc procedure contains series of nobler elements than zinc, whereby their content in accordance with the concentrates and other components varied. Most important bottom them are coppers, cadmium, cobalts, nickels, arsenics, antimonies, germanium and thallium. Because these elements are nobler than zinc, they are inclined to separate with the electrolysis on the cathode. This is not desired, because they contaminate the deposited zinc, and because some these elements side reactions (hydrogen development) cause.

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Because the aforementioned elements are nobler than zinc, one can cement them from the solution by metallic zinc. This method becomes almost exclusively used, however with the exception of the method of the solution cleaning, during the zinc production, where the nobler metals than zinc become from that zinc electrolytes remote with the help of an extraction with b-Naphtol.

Although the zinc metallic during the solution cleaning used general

cementing means is, some auxiliaries normally become, like z. B. Arsenic or antimony used. With the use of antimonies the cleaning stages are generally continuous working steps, so that the first step covers the removal of cadmium and copper and the second step the removal of cobalts and nickels; the second possible step is thereby a major support stage for the preceding method.

In principle exist two different methods, which begin as auxiliary of zinc arsenic. In accordance with the former method become from that zinc electrolytes in the first step of the solution cleaning coppers, cobalts and nickels either in the batch method or remote in the continuous working method. The second step is the removal of cadmium, and the third step - if necessary - becomes used as support stage for the method.

In accordance with the second solution cleaning method using arsenics as auxiliary of zinc the solution cleaning in three steps takes place, of which first and the third step are generally continuous and the middle stage an automatic batch method. In the first step that becomes major portion of the copper of zinc electrolytes the separated. In the second step the remainder of the copper as well as cobalts, nickels and germanium becomes separated. In the third step major cadmium becomes separated.

The second step (the batch method) in a three speed solution cleaning method using arsenics as auxiliary becomes conducted normally as follows: Feeding zinc electrolytes into the reactor becomes started. If the reactor is for example half full, started becomes and feeding zinc powder can begin with mixing. First made feeding of the powder quite rapid, in order to achieve in the reactor sufficient content. Against end of the reactor filling procedure feeding becomes slowed, however still continued until the total amount of the zinc calculated for the approach is added. After a given time interval a CO analysis becomes conducted for the solution, and if this shows that cobalt is in a sufficient amount deposited, is the approach finished. If the result of analysis is insufficient, the feed with powder up to reaching an appropriate cobalt separation becomes continued. The obtained deposition does not become remote after each deposition, on the contrary successively several depositions become conducted, whereby the deposition becomes only from time to time remote.

Proportioning the zinc powder has a major problem shown. General one became a "sufficient" powder quantity reaching a good end result added. Even small troubles lead normally to an increase with the use of the powder and the return to the earlier smaller additions large efforts required. With other words there was no suitable indicator for the suitability of the fed powder.

It is already for a long time known that the precipitation of the subsequent equation obeys:

EMI 5.1

whereby  $k$  = coefficient of the deposition rate  $t$  = separation time  $CO$  = initial contents  $C_t$  = content with the run time

After this equation the deposition takes place then, if in the reactor the proper conditions are present, the amount at zinc powder sufficient is etc. It becomes however shown that a increase of the addition in powders over the point of the "sufficient amount" outside the deposition not accelerated. On the other page an excessive use of the powder can even slow the reaction down, whereby the reason for it is the formation of alkaline zinc sulfate.

In the Finnish publication writing 66,027 a solution cleaning method for zinc electrolyte described becomes, becomes so adjusted with which with the removal of coppers the required amount at zinc powders that it corresponds to the approximate stoichiometric amount, which is required to the removal of the copper from the solution. The addition of zinc powder can become with the help of the redox potential of the electrolyte solution adjusted. The redox potential becomes the control of the addition of zinc powder so adjusted that the potential electrolytes within the range from +200 to -600 mVs maintained becomes. The used redox range the defined extent of the copper distance and limited separating of other metals. The solution, is remote from which copper, becomes the other removal of cobalts supplied.

In the publication of Sawaguchi et. aluminium "Zinc Electrolyte Purification RK Ijima zinc Refinery", MMIJ/AusIMM Joint symposium 1983, Sendai, S. 217-229, it is pointed out that adjusting the germanium content the adjustment of a potential used became, in order to make the germanium level in the electrolyte solution in the second step of the solution cleaning sufficient low. If the potential becomes corresponding within the range of -610 to -640 mVs adjusted, the germanium level can become below 10 ppm maintained.

In the aforementioned publication the measurement of a redox potential became used, in order to adjust the extent of the removal of the metal which can be removed from the solution. This is natural regarding the quality of the final product an important factor. Another factor, that the production costs of zinc affected, is the zinc powder quantity used during the solution cleaning. As became from the Finnish publication 66,027 significant, z corresponds. B. with the removal of the zinc powder the coarse stoichiometric amount admitted by copper the initial amount, according to which the powder becomes added in accordance with the requirements of the situation. It applies that the mentioned publication reflects the adjustment of the additions with the assistance of the redox potential mentioned, on the other hand one the specified range (+200 to -600 mVs) again that the mutual dependency between the addition and the potential remained unclear.

According to invention the addition of zinc powder can become during the solution cleaning of zinc electrolyte so adjusted in particular by redox potential measurements that it remains within the optimum range. The essential characteristic features of the invention become from the appended claim 1 significant.

In the second step of the solution cleaning - during the so called cobalt

distance - the copper remained after the removal of coppers becomes from the solution as well as cobalts, nickels and germanium deposited. The subsequent table shows the amounts of the elements, which occur the second step of the applied solution cleaning. The remainder contents of the solution contained from the second step must be small extreme:

EMI 7.1

As foregoing performed became, metallic zinc powders and  $\text{As}_2\text{O}_3$  become used with the deposition. The separation procedure follows the subsequent

reaction equations:  $\text{Cu}^{++} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{++}$  (1)

$6 \text{Cu}^{++} + \text{As}_2\text{O}_3 + 9 \text{Zn} \rightarrow 2 \text{Cu}_3\text{As} + 9 \text{Zn}^{++}$  (2)

$2 \text{ME}^{++} + \text{As}_2\text{O}_3 + 5 \text{Zn} \rightarrow 2 \text{MeAs} + 5 \text{Zn}^{++}$  (3)

ME = CO, Ni

The deposition of germanium is unknown. As side reaction resolution of Zn-powder takes place:  $\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2$  (4)

$x \text{Zn} + \text{ZnSO}_4 + (x + y) \text{H}_2\text{O} \rightarrow \text{ZnSO}_4 \cdot x \text{Zn}(\text{OH})_2 \cdot y \text{H}_2\text{O}$  (5)

The arsenic quantity becomes adjusted in simple way in accordance with the initial content. Consequently the use of a too low leads or to large quantity to difficulties with the deposition or with an high Endgehalt at arsenics.

Now surprisingly shown has itself that one can keep optimum deposition conditions without the use of excessive amounts at Zn-powders by adjusting the amount at admitted Zn-powder with the help of the redox potential. Simultaneous one points the measurement to also possible troubles out with the addition of powder. The invention becomes subsequent bottom reference on the accompanying drawing described, are graphic explained in which the essential features of the invention; it shows:

Fig. 1 the cobalt distance from the electrolyte solution with different values of the redox potential as function of time;

Fig. 2 the removal of nickels in same way as above; and

Fig. 3 the removal of germanium in same way as above.

From the drawing significant becomes that the maximums become already with the deposition of cobalts and nickels with the potential -575 mVs achieved. The maximums with the deposition of germanium fall into the range from -600 to -625 mVs. The redox potential became with a platinum electrode measured, the used reference electrode was a calomel electrode.

With to it the employees research work it was found that one can decrease the amount of the used Zn-powder in simple way up to the half that by adjusting the addition of powder by potential measurements early used amount, whereby the extent at impurities remains the same. This means that the production capacity of a plant can become essential increased, whereby the achieved use can become calculated in accordance with the gain, if the electrolysis is the limiting factor of the method. The reduction of the production costs of zinc powder means a considerable use alone likewise.

In accordance with the new adjusting procedure the addition at Zn-powders becomes adjusted into the reactor by redox potential measurements during the durations of filling the reactor with the second step of the solution cleaning on a certain value. The amount of the fed powder becomes a so chosen that together with the solution into the reactor incoming  $\text{Cu}^{2+}$  the Kobaltarsenid or the Nickelarsenid of the deposition already present in the reactor does not solve, however copper deposited becomes. On the other page the addition at zinc powders must be like that that the Zn-powder does not separate and that no arsine formed becomes, although the solution contains also arsenics. If arsine becomes formed, it is this as such because of the environmental endangerment hazardous, leads however beyond that naturally to increased consumption to Zinkpulver. Wir could show that is smaller considerable with the use of the potential attitude the amount at arsine, which becomes released together with the waste gases than before. This is to be attributed to the fact that the potential now none so low value achieved that the generation of arsine would be possible. In the practice it has itself shown that it represents a good solution in this step, to adjust the redox potential within the range from -480 to -550 mVs against the calomel electrode. If the reactor is full, the copper remained after the first step of the solution cleaning in the solution becomes likewise remote in accordance with the foregoing description. Afterwards the addition of zinc powder becomes so adjusted that the deposition of cobalts, nickels and germanium begins. In practice this potential range amounts to -570 to -650 mVs against the calomel electrode. Each impurity has its own potential range, whereby the amount at old deposition the optimum range affected present in the reactor.

With use of the redox potential measurement it is thus possible in such a way to stop the addition at zinc powders that the desired potential will maintain and that these metals become deposited, however a simultaneous excessive use at Zn-powder avoided becomes. If the contents of the solution which can be fed into the reactor concerning the various impurities just as known is as the amount on in the reactor after the preceding approaches present deposition, it is possible to define the separation time experimental according to which the feed with powder becomes stopped.

Foregoing one became adjusting the redox potential in the second step of the solution cleaning described, where the method becomes operated as batch methods. Adjusting of the redox potential can become however also with a continuous process realized. Corresponding one can take place the removal from cobalts on continuous manner or one can an adjusting of the redox potential in other steps of the solution cleaning use.

In the foregoing description the invention became major described regarding a method, which arsenic begins as auxiliary. One points out however that one can apply the method also to methods, which use other auxiliaries, whereby it agrees complete with these Verwendugn with the thought the instant invention. The optimum values of the redox potential can vary compared with the foregoing data slight, not however in essential

circumference.